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Comparing Measured and Modelled PFOS Concentrations in a UK Freshwater Catchment

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Abstract

The lifecycle, sources and fate of perfluorooctane sulfonate (PFOS) continues to generate scientific and political interest, particularly since PFOS was listed by the Stockholm Convention and largely restricted in Europe. It continues to be detected in aquatic environments, with only limited studies into the on-going sources. This paper explores PFOS emissions discharged by the general population into a small catchment comprising of two rivers in the UK. A sampling campaign was undertaken to improve our understanding of population-derived PFOS sources from sewage treatment plants (STPs) and in rivers. A corresponding modelling exercise allowed an emission estimate of 13 µg/day/per capita to be derived for the Aire and Calder rivers. PFOS emission was linked to STP discharges, and thereby population density, by using a correlation with the artificial sweetener sucralose, a conservative chemical marker for waste water (R^2 = 0.69). The model was able to accurately estimate the spatial trends of PFOS in the rivers, while predicted concentrations were within a factor of three based on per capita emission values taken from the literature. Measured PFOS concentrations in rivers suggested that emissions from STPs are partially dependent on treatment type, where plants with secondary or tertiary treatment such as activated sludge processes emit less PFOS, possibly due to increased partitioning and retention. With refinements based on the type of treatment at each STP, predictions were further improved.

The total PFOS mass discharged annually via rivers from the UK has been estimated to be between 215 and 310 kg, based on the per capita emissions range derived in this study.

Keywords

Perfluorooctane sulfonate, Modelling, Monitoring, River Aire, Stockholm Convention, Emissions.

Abbreviations

GLRM, General linear river model; LOQ, Limit of quantification; MEC, Measured environmental concentration; PEC, Predicted environmental concentration; PFBS, Perfluorobutane sulfonate; PFAS, Perfluoroalkyl and polyfluoroalkyl substances; PFOA, Perfluorooctanoic acid; PFOS, Perfluorooctane sulfonate; STP, Sewage treatment plant.

1. Introduction

Perfluorooctane sulfonate (PFOS) is of continuing interest to environmental regulators due to its widespread dispersion in aquatic environments. Despite the major global manufacturer (3M) phasing out production in 2002, and subsequent introduction of European and international restrictions or regulations on use (including the European Directive 2006/122/EC and the addition of PFOS to Annex B of the Stockholm Convention), PFOS continues to be found widely dispersed in fresh (de Voogt et al., 2006; Loos et al., 2008a; Möller et al., 2010) and salt water (Wei et al., 2007; Yamashita et al., 2008; Ahrens et al., 2009b) environments. Considering the phase-out of production and subsequent restrictions, PFOS emissions in Europe are believed to now arise primarily from consumer use and wastes, and should therefore be intrinsically linked to population. Indeed, 3M suggests that 85% of emissions arise during the consumer lifecycle (3M, 2000), whereby products emit a proportion of their treatment through use, cleaning (washing) and disposal or recycling, principally to waste waters and solid wastes. Consequently from 2002 onwards, there remained a substantial reservoir of products treated with perfluorooctanesulfonyl fluoride (POSF)-derived chemicals which included PFOS in use. Although this reservoir is now expected to be decreasing, emissions are projected to continue for some time as products near the end of their useful life. A recent study by Möller et al. (2010) suggested that PFOS is no longer the dominant perfluorinated compound found in freshwater environments, with its replacement perfluorobutane sulfonate (PFBS) now dominating the emission pattern. However, PFOS has recently been listed in the European Directive 2013/39/EU as regards priority substances in the field of water policy, while understanding of emissions from diffuse populations remains limited.

Zareitalabad et al. (2013) provide a thorough review on global PFOS concentrations in surface waters and STP effluents. They find the median surface water concentrations for Italy (Loos et al., 2008b), Austria (Clara et al., 2009) and Germany (Ahrens et al., 2009b; Ahrens et al., 2009a; Möller et al., 2010) to be 5, 11 and 5 ng/L respectively, with a maximum of 5,900 ng/L measured in Steinbecke, Germany (Skutlarek et al., 2006). Sewage treatment plants (STPs) are known to be major sources of PFASs to the aquatic environment. Ahrens et al. (2010) found PFAS concentrations 5-10 times higher in STPs effluents than in the surface waters for the River Elbe, Germany. Schultz et al. (2006) calculated the average mass flow of both PFOS and its precursors over 10 days throughout a STP; PFOS was found in both the dissolved phase and in sludge. The average mass flow increased significantly across the trickle filter, with further increases most likely as a result of degradation of precursors during the activated sludge process. It was estimated that 2.5 times more PFOS left the plant in the final effluent than remained in the anaerobically digested sludge. Similarly, Becker et al. (2008) reported that PFOS levels increased 3 fold in the liquid phase and 9 fold in the particle phase during STP treatment, which resulted in the retention of almost half the PFOS burden by the activated sludge in Bayreuth, Germany. PFOS levels were lowest in grit and highest in sludge, resulting in around 55% released into the river water, while 45% was retained in the dewatered, deactivated sewage sludge.

Several authors have since attempted to derive PFOS per capita emissions for population; Pistocchi and Loos (2009) reported a value of 27 µg/day as a European average, Becker et al. (2008) reported 40 µg/day for a German STP, while Schultz et al. (2005) and Huset et al. (2008) gave values of 42 µg/day and 57 µg/day for outflows from US and Swiss STPs respectively. Previously in Paul et al. (2011) we explored the link between per capita emissions and measured concentration profiles in the River Rhine. The modelling exercise indicated that per capita emissions multiplied by population can be used to accurately estimate PFOS concentration trends within a European river system, even if predicted concentrations were generally within a factor of two of measured environmental concentrations. Despite the apparent retention and partitioning in STPs (Schultz et al., 2006; Becker et al., 2008), the exercise identified that the likely K_d range of PFOS applicable to freshwater environments without artificial mixing was less than 10 (log L/kg), and that degradation is not a relevant environmental process due to the known chemical stability of PFOS. A previous study with similar aims investigated endocrine disruptors in the catchment, and suggested model predictions can provide information that compares well with good

quality chemical measurements (Sumpter et al., 2006; Johnson et al., 2008). This study aims to predict environmental concentrations of PFOS in a UK freshwater catchment using a general linear river model with inputs derived from population density data and a per capita emission rate. PECs are compared with monitoring data for validation and several alternative emission distribution methods are explored.

2.1 Methods

2.1.1 The Study Area and River Model

A general linear river model (GLRM) previously used in Paul et al. (2011) and Blaser et al. (2008) for the River Rhine, was reparameterised to individually represent the Aire and Calder rivers in Yorkshire, UK (Figure 2). This catchment was chosen due to its well documented hydrological information and history of aquatic pollution modelling using the GREAT-ER model (Keller et al., 2006; Sumpter et al., 2006; Johnson et al., 2008). Information vital for model set up including water flows and volumes was available from the UK Environment Agency (Environment Agency, 2010). Annual averaged flow rates for both rivers were compiled for the gauging stations. Annual discharge of the River Aire and Calder were 35.1 m^3/s and 19.7 m^3/s respectively for 2010. Discharge in April 2010 and May 2013 were much lower than the annual average, by 48% - 86% across the nine gauging stations, and generally May has the lowest monthly discharge. It is, therefore, very likely that target chemical concentrations will be higher in May than other months, assuming constant emission rates. Conversely, surface run-off and STP discharge rates will be lower. Precipitation in the week before sampling in May 2013 was low at 8.3 mm/week and 2.5 mm/week in the Aire and Calder catchments respectively and there was no precipitation on the days of sampling (averaged from five locations in each catchment; www.worldweatheronline.com).

Each river was digitised in ArcMap and divided into stretches of 5 km in length, with each stretch representing a box of the river model. The Aire was modelled using two sections: a pre-confluence section of 20 boxes in length (100 km) and a post-confluence section of 10 boxes (50 km). The Calder is modelled using 15 boxes. The Calder joins the Aire in the first box of the post confluence model. Water velocity (1 m/s) and river depth (1 m) are set to be constant, while volume is determined by the width of the river. For the Calder and Aire pre-confluence sections, the width of the river increases linearly from 2 m to 8 m and 9 m respectively. Both rivers discharge into the post confluence model to a flow of 17 m^3/s in the first section and and remain constant thereafter.

Each box consists of a compartment of moving water (W1), a compartment of stagnant water (W2) and a compartment representing the top layer of the sediment (Sed). The volume of the sediment was calculated at 5% of the stagnant water, which was in turn set to 12.5% of the moving water body. The compartments are assumed to be completely mixed, i.e. steady state. The model includes the following advective and reactive processes; degradation, downstream transport of dissolved and particle-bound PFOS with moving water; bulk exchange between moving and stagnant water; sedimentation and resuspension of particles to and from moving water and burial of particles into the permanent sediment. Figure 1 shows the structure of each model compartment including transport and fate processes. Table S6 describes the parameters used in the model and Table S7 provides a simple sensitivity analysis of those parameters.

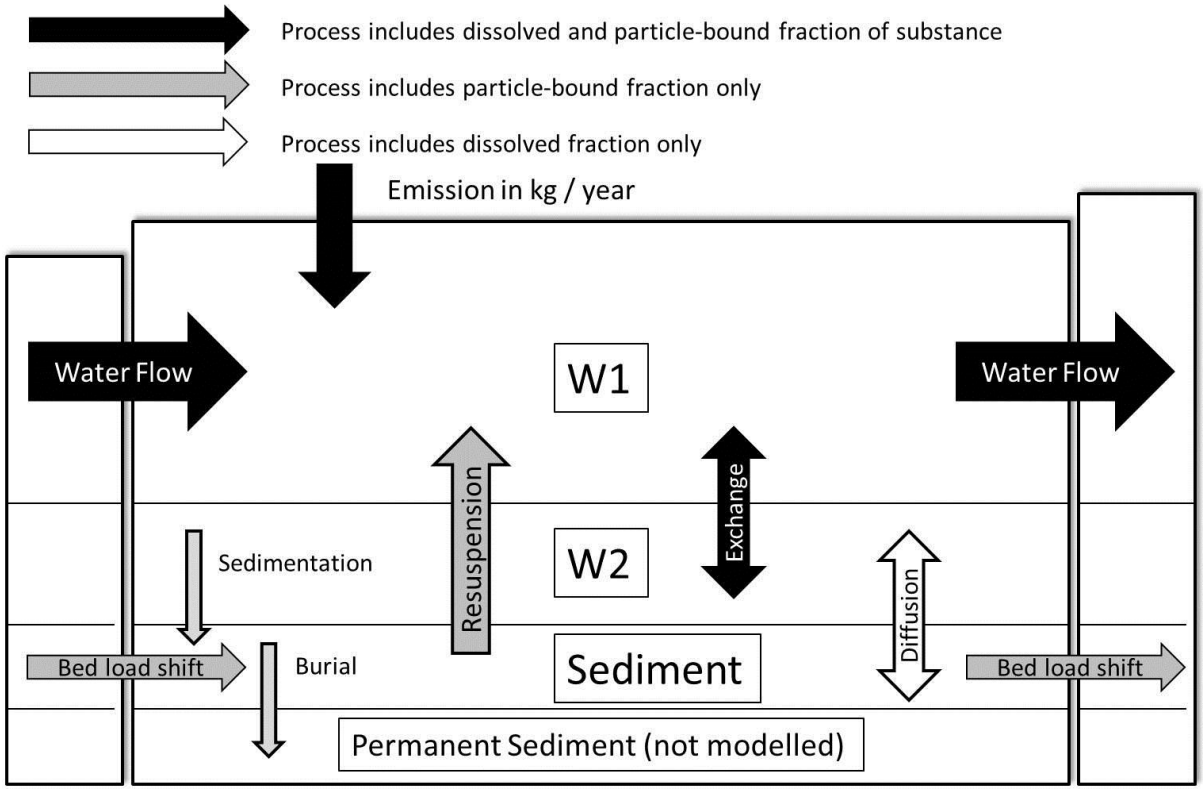


Figure 1: Processes simulated in the Aire and Calder models. W1 is the moving water, W2 the stagnant water and Sediment represents the top layer of the sediment. Adapted from Blaser et al., 2008.

2.1.2 Population derived emissions

The population count and model inputs were generated using a Eurostat population dataset in ArcGIS. The population in the vicinity of the Aire and Calder rivers is well contained by the topography of the catchments (Figure 2). The River Aire and Calder have catchment areas of

282 km^2 and 341 km^2, respectively. Initially, modelled PFOS emissions per box in kg/year were estimated by multiplying the population per river box by a per capita emission rate of 27 µg/day estimated by Pistocchi and Loos (2009). Emission estimates were then refined further, using methods detailed below. Approximately 1.2 million people live within the catchment of the River Aire, which passes through the large cities of Bradford and Leeds, while 700,000 people live within the catchment of the River Calder which passes through Halifax, Dewsbury and Wakefield before merging with the River Aire.

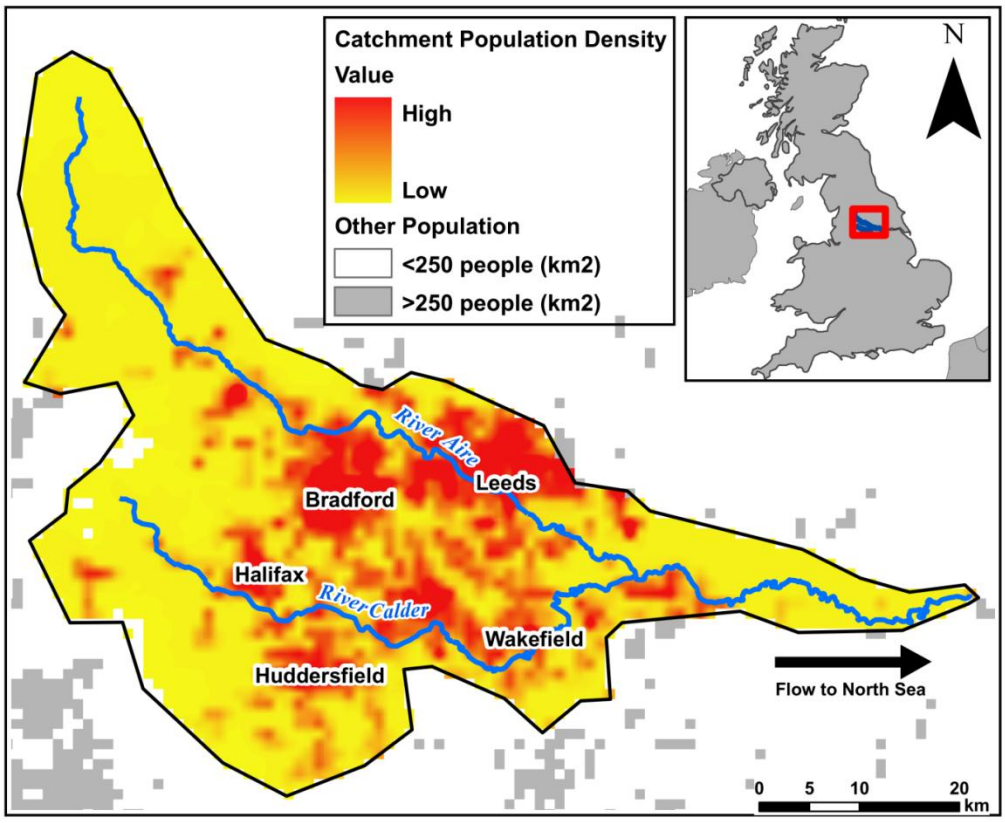


Figure 2: Location of the Aire and Calder rivers, the catchment area and major conurbations with population density.

2.1.3 Emission Scenarios

Paul et al. (2011) established that partitioning and degradation are not major loss mechanisms for PFOS (<6%), particularly in rivers with short residence times and that population can provide a reasonable indication of emission trends. Based on these results, we test the hypothesis that PFOS concentrations in the Aire and Calder rivers can be accurately modelled using population density and the European average per capita emission rate proposed by Pistocchi and Loos (2009). Population density is a common metric often freely available in detailed density maps compatible with GIS software, making it ideal for deriving model

inputs, unlike the much less accessible STP data. It is also relatively fast and simple to re-parameterise this particular model to simulate any other catchment of interest, given that some basic hydrographical parameters are known. Secondly, we test an alternative hypothesis that point releases from STPs can better predict concentrations by deriving inputs from the population served by each STP on the rivers, rather than population density. In this scenario the type of STP treatment is also considered (activated sludge is 4.3 times more effective at removing PFOS than trickling filter alone). Finally, we apply a reverse modelling method to calculate the inputs required to meet the concentrations measured in the river, such that PECs equal MECs for all locations. This allows a comparison of population and STP derived inputs with the 'best-fit' inputs to assess the suitability of population density based modelling. Model inputs for the River Aire and Calder are shown in Tables S4 and S5, respectively.

Model inputs:

(i) **Population density inputs** - mass inputs derived from population density of the box multiplied by the EU average per capita emission rate (27 µg/day/person).

(ii) **STP population served** – mass inputs derived from the population served by each STP multiplied by the EU per capita emission rate.

(iii) **STP type adjusted** – same as (ii) but correcting emission rates for different STP type. Two types of STP, standard and activated sludge with higher removal efficiency of PFOS (4.3:1).

(iv) **Reverse modelling** – reverse modelling to generate PECs that match MECs and 'best-fit' model inputs.

2.2 Sampling Campaign and Methods

2.2.1 River Sampling

Two sampling campaigns collected water samples from the Aire and Calder rivers on consecutive days in April 2010 and May 2013 (Table S2 and S3) to provide the monitoring data for model validation and assess variability in concentrations.

In April 2010, samples were collected at least 1 km downstream of the STPs to allow sufficient mixing of effluent with river water and were collected using 1 L glass bottles (Schott-Duran) either lowered from a suitable bridge by rope, or by telescopic pole from the river bank. Where possible, samples were taken in the middle of the stream at an approximate

depth of 30 cm. Samples were then transferred into 500 mL pre-washed (methanol) Nalgene HDPE bottles and stored chilled at 4°C.

In May 2013, sampling locations were adjusted with consideration to accessibility, targeting upstream and downstream of the major STPs and near the confluence of the River Aire and Calder. We also sampled an STP effluent discharge stream on the River Aire. Samples were collected in 2.5 L amber glass bottles (pre-washed twice with methanol). Samples were then transferred into 500 mL pre-washed (methanol) Nalgene HDPE bottles and stored chilled at 4°C.

2.2.2. Sample preparation, analysis and QA/QC

Sample analysis was performed at the Joint Research Centre (JRC), Ispra, Italy, two weeks after sampling in the last week of April 2010 and in May 2013. The water samples were stored and transported using 500 mL HDPE bottles (cleaned with methanol). They were transported under cooled conditions (4°C in thermostatic boxes) within 48h to the JRC.

Experimental details are given in Loos et al. (Loos et al., 2008b; Loos et al., 2009a; Loos et al., 2009b; Loos et al., 2010a; Loos et al., 2010b; Loos et al., 2013). In short, water samples were not filtered, but decanted in the laboratory. Before extraction, samples were spiked with the isotopically labelled internal standards $^{13}C_4$-PFOS (at 10 ng/L; *Wellington Laboratories*, Guelph, Ontario, Canada), and sucralose-d6 (1 µg/L; *Spectra2000*, Rome, Italy), and then processed by solid-phase extraction (SPE) using an *AutoTrace*© SPE workstation (*Tekmar-Caliper Life Sciences-Thermo*); 400 mL of unfiltered water was extracted with *Oasis*© *HLB* SPE cartridges (200 mg; *Waters;* Milford, MA, USA) at a flow rate of 5 mL/min; after extraction they were dried with nitrogen in 30 min; elution was performed with methanol (6 mL); then the extracts were evaporated to 500 µL (in 2010) under a stream of nitrogen using a *TurboVap*© *II Concentration Workstation* (*Caliper Life Sciences*; now a *PerkinElmer* company; Hopkinton, MA, USA) in a water bath at a temperature of 40°C. In 2013, the extracts were evaporated to dryness and reconstituted in 200 µL of a 90:10 % (v/v) mixture of 5 mM ammonium acetate and 50:50 % acetonitrile - methanol (v/v).

Liquid chromatography electrospray ionization (ESI) tandem mass spectrometry (LC-MS/MS) was used to analyse the samples. In 2010, the samples were analysed with an *Agilent Technologies* (Santa Clara, CA, USA) 1100 HPLC coupled to a *Waters* (Milford, MA, USA) *quattro micro* triple-quadrupole MS-MS (Loos et al., 2008b; Loos et al., 2009a; Loos et al., 2009b; Loos et al., 2010a; Loos et al., 2010b). In 2013, a *Waters Acquity*©

UHPLC system coupled to a hybrid triple-quadrupole linear ion trap mass spectrometer (5500 *QTRAP*©) with a turbo ion spray source from *AB SCIEX* (Foster City, CA, USA) were used (Loos et al., 2013). Both MS systems were operated for quantification under selected reaction monitoring (SRM) acquisition mode. The SRM transitions used were: PFOS m/z 499 > 80 and 99; $^{13}C_4$-PFOS m/z 503 > 80 and 99; sucralose m/z 395 > 359; sucralose-d6 m/z 401 > 365. Reversed-phase LC separations were performed in 2010 with a *Hypersil Gold* column (*Thermo Scientific*, 100 × 2.1 mm, 3 mm), and in 2013 with a BEH C18 analytical column (*Waters*) 50 × 2.1 mm, 1.7 mm.

Analytical quality control measures (QA/QC) were described before (Loos et al., 2008b; Loos et al., 2009a; Loos et al., 2009b; Loos et al., 2010a; Loos et al., 2010b; Loos et al., 2013). Recoveries of PFOS and sucralose were around 60%. They were corrected with the help of the internal standards. Good drying of the cartridges is important for high PFOS recoveries. The limits of detection (LODs) for the SPE-LC-MS/MS procedures were calculated according to ISO/TS 13530 (2009) from the mean concentration of laboratory blank water samples (50 mL of Milli-Q water) plus three times the standard deviation. The limits of quantification (LOQs) are usually 3 times the LOD (LOQ = 3 × LOD). For PFOS, the blank value dependent LOQ was around 0.3 ng/L using the *quattro micro* instrument (Loos et al., 2008b), and 0.086 ng/L with the 5500 *QTRAP*© (Loos et al., 2013). For sucralose, the LOQ was around 10 ng/L (Loos et al., 2009a) and 0.221 ng/L (Loos et al., 2013), respectively. In addition, the JRC participated in several international interlaboratory studies on perfluoroalkyl compounds (van Leeuwen et al., 2009).

3. Results and Discussion

3.1 PFOS Sampling Results

PFOS was detected in all river samples collected in 2010 and 2013, although five samples from 2013 were below limit of quantification (<LOQ). Figures 3 and 4 show the trend in PFOS concentration in the River Aire and Calder respectively. Tables S2 and S3 present all sampling results. In both rivers, PFOS concentration generally increases further downstream from the source with slight decreases in concentration in several locations. The decreases in concentration can be largely explained by dilution from the input of freshwater streams. The maximum PFOS concentrations measured in the Aire and Calder were 17.2 ng/L and 20.7 ng/L respectively, both in 2013. Levels in 2010 were 2-3 ng/L lower, with maximums in the Aire and Calder of 11.3 ng/L and 14.7 ng/L, respectively. Zareitalabad et al. (2013)

summarised reported PFOS concentrations from European studies, finding a median concentration of 7 ng/L in river waters, in good agreement with our own results (Figure S1).

PFOS was also measured in an effluent sample collected in 2013 at 13.5 ng/L, lower than other European STP effluents (median 49 ng/L), but within the range of reported values (Zareitalabad et al., 2013). This particular STP from which the effluent was collected is the largest in the catchment, serving over 600,000 people and is potentially the dominant source of pollutants to the River Aire. Comparing 2013 PFOS concentrations, upstream and downstream at each of the major STPs on the River Aire, shows increases in concentration after every STP, with the exception of Whedale STP (99 km). In 2010, a decrease between Esholt STP (60 km) and Kirkstall (70 km) was observed, probably due to dilution by freshwater inputs from small tributaries. A similar pattern in PFOS concentrations increasing after every STP is also observed in the River Calder, with the exception of Wakefield STP. Here, PFOS concentration decreases from 20 ng/L upstream to 13.2 ng/L downstream and cannot be explained by dilution as there are no significant freshwater inputs between the two locations.

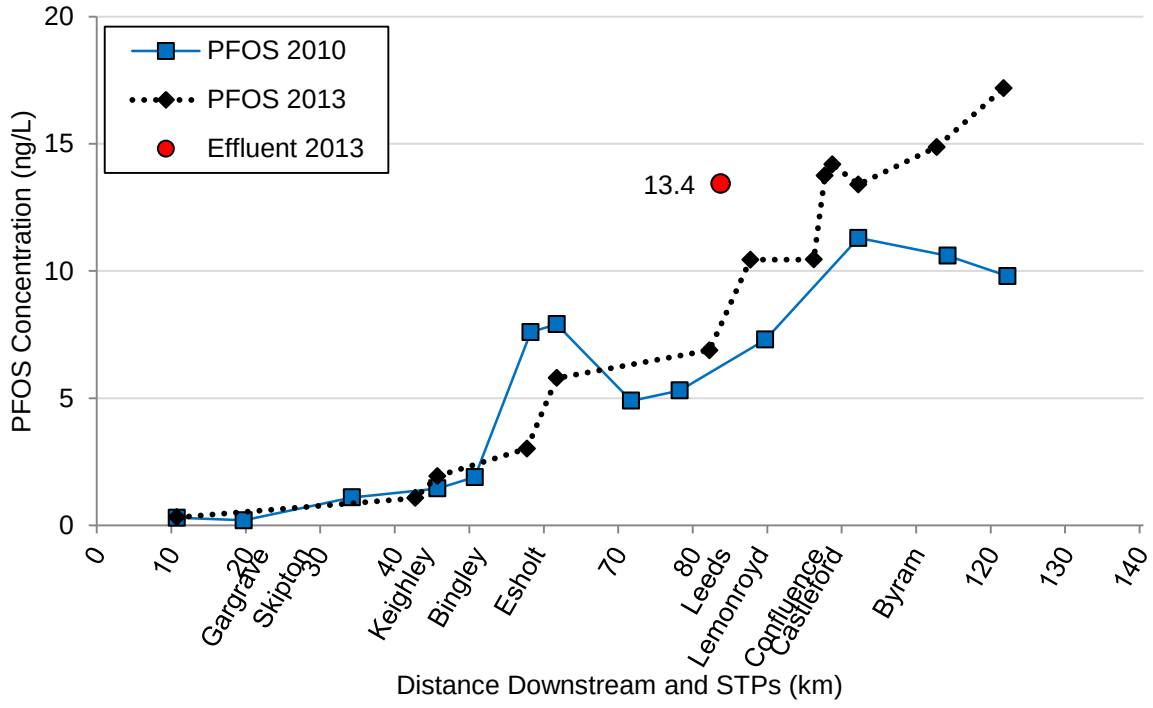


Figure 3: River Aire April 2010 and May 2013. Calder input at 96.5 km. PFOS concentrations in the River Aire increase after every STP with the exception of Castleford STP (101 km) where concentration drops slightly. The effluent concentration from Leeds STP is shown clearly.

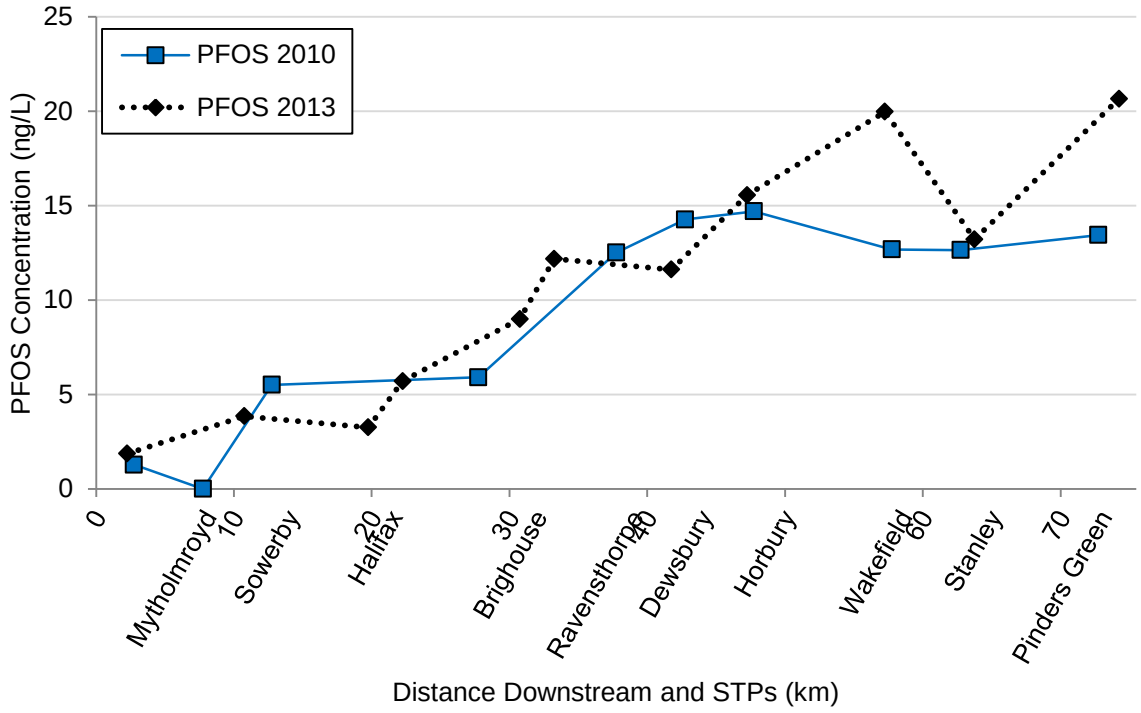
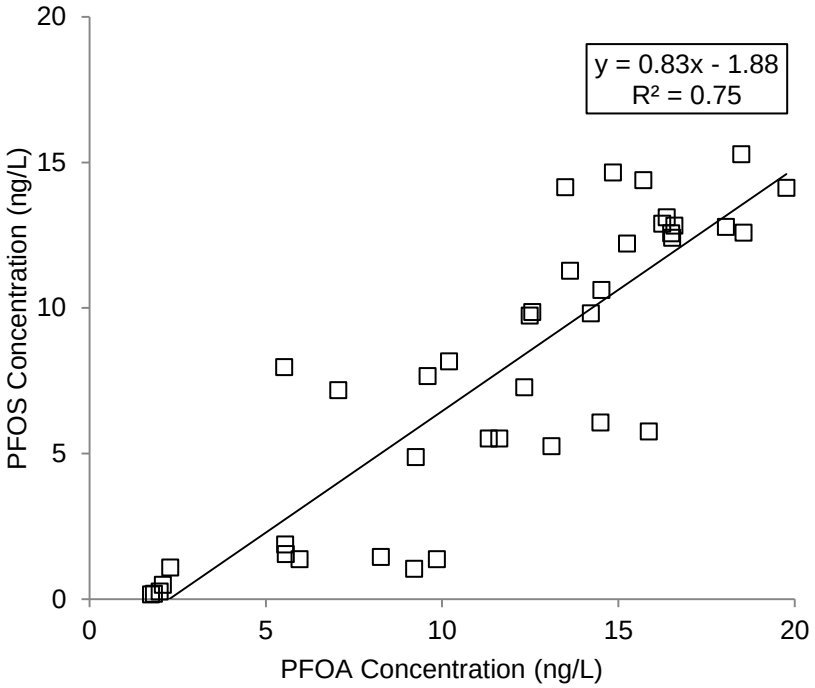


Figure 4: River Calder April 2010 and May 2013.

3.2 PFOA and Sucralose

Water samples were also analysed for PFOA (2010 only) and sucralose. Overall, concentrations of both chemicals were slightly higher in the River Calder than the River Aire, and levels in both rivers were very similar in 2010 and 2013. Generally, PFOA concentrations were higher than PFOS by several ng/L in both rivers, with a maximum PFOA concentration measured near Dewsbury and Wakefield. Surprisingly high levels, nearly 10 ng/L, were measured at the background site and background concentrations were also higher on the Aire. This suggests there may be significant input from an unknown source, possibly atmospheric deposition in this catchment. Linear regression of PFOS and PFOA concentrations gives a good linear correlation, R^2 = 0.75, and a good log-log R^2 = 0.82 suggesting both chemicals are emitted at similar locations at similar rates. The intercept does not pass through the origin, but where PFOA = 2.6 ng/L supporting the idea of additional indirect sources of PFOA.



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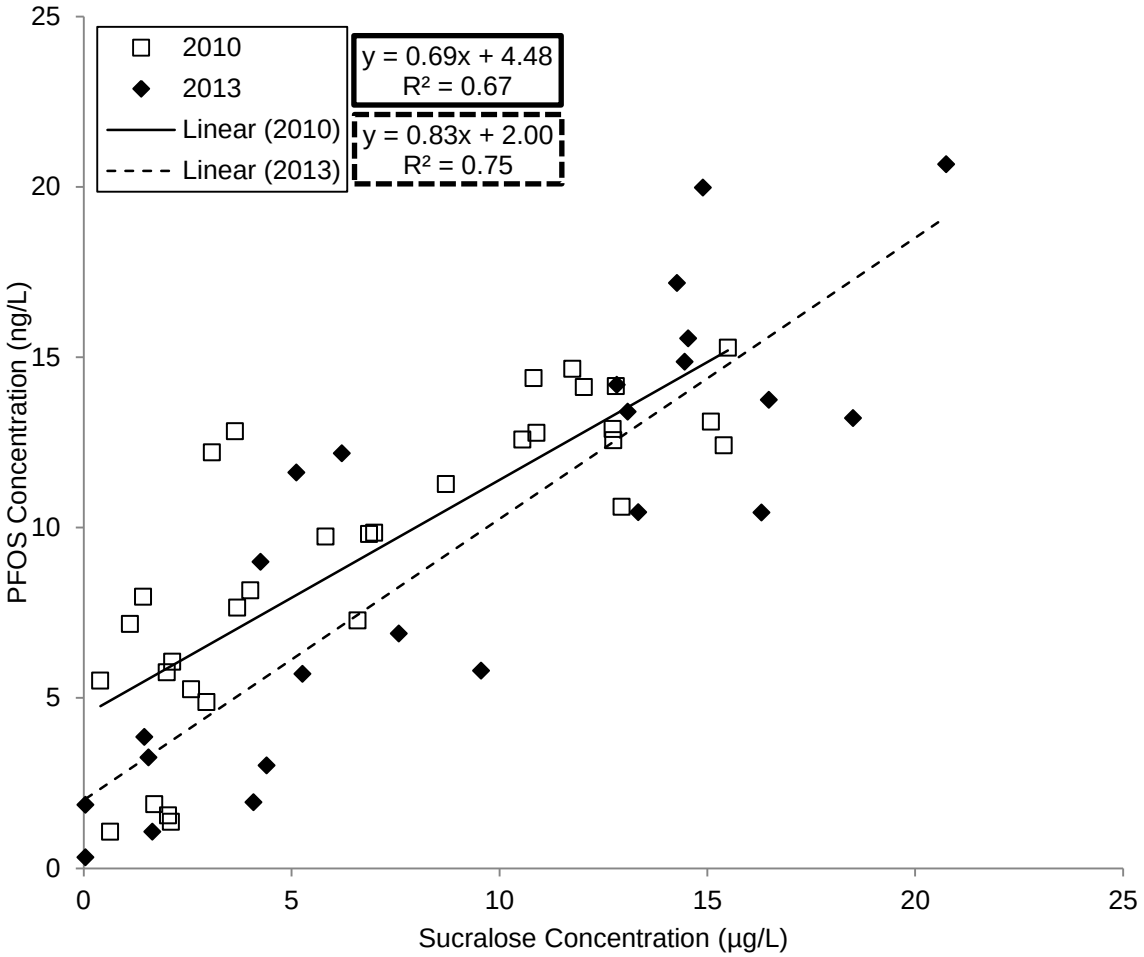
300 **Figure 5: Measured PFOS vs PFOA concentrations from 2010 (n=40).**
301

302 Sucralose concentrations were in the µg/L range, three orders of magnitude higher than PFOS
303 concentrations. In 2010, sucralose concentrations ranged from 0.4 -15.5 µg/L with higher
304 levels measured in the River Calder. In 2013, concentrations were generally similar with a
305 maximum of 20.8 µg/L on the River Calder. These levels are higher than receiving and
306 surface water concentrations summarised by Tollefsen et al. (2012) which indicates higher
307 sucralose consumption in the UK compared to other countries. They found surface water
308 concentrations of sucralose to be in the range of 1 – 1,900 ng/L. Similarly, levels in
309 Switzerland are over an order of magnitude lower (Berset and Ochsenbein, 2012). The
310 effluent sample collected near Leeds had the highest concentration of sucralose, 30.5 µg/L,
311 and is likely responsible for a doubling of concentration observed in the River Aire. Linear
312 regression of PFOS and sucralose concentrations gives a good correlation, R^2 = 0.67 (2010)
313 and R^2 = 0.75 (2013). Scheurer et al. (2009) and Berset and Ochsenbein (2012) reported
314 sucralose concentrations in effluents in the range 0.07 – 16 µg/L, slightly lower than our own
315 finding, although higher concentrations have been observed (Oppenheimer et al., 2011). This
316 is a clear indicator of the importance of STPs as point sources for sucralose and high
317 consumption in the UK.



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319 **Figure 6: Measured PFOS (ng/L) vs sucralose (µg/L) concentrations**
320 **(2010 n=32, 2013 n=24).**
321

322 ### 3.3 Comparison of Measurements with Modelled Concentrations

323 Figure 7 shows the modelled versus the measured PFOS concentrations in the Aire and
324 Calder rivers. It demonstrates that spatial concentration trends can be reasonably well
325 predicted based on population derived inputs. Estimated PFOS concentrations in the Aire
326 were overestimated by up to a factor of 4 using population density and a per capita emission
327 rate of 27 µg/day (Figure 7). Results based on the EU average emission from reference
328 (Pistocchi and Loos, 2009) are shown on the right-hand y-axis to avoid distortion of the
329 remaining figure, and better highlight the overall environmental concentration trend. This is
330 consistent with the estimates made for the River Rhine (Paul et al., 2011). When inputs are
331 derived from STP population served and location, PECs decrease slightly, but remain 3-4
332 times higher than MECs (not shown). However, correcting for STP type, estimated
333 concentrations agree very well with MECs. The general trend in PECs also agrees better with

MECs, that is, concentrations increase after every STP discharge. This result suggests that MECs cannot be accurately predicted using a single per capita emission rate and population density. Using the STP type approach improves the spatial accuracy of emissions, takes account of STP removal efficiency and improves model predictive power. A similar improvement could be made for the population density inputs by decreasing the per capita emission rate from 27 µg/day/person to approximately 10 µg/day/person.

Results for the River Calder are similar to those of the Aire. Inputs based on population density and the EU average emission rate results in overestimation of MECs, but within a factor of 2. Adjusting the inputs to STP type improves the concentration trend and the absolute PFOS concentrations, although now slightly lower than the MECs by several ng/L.

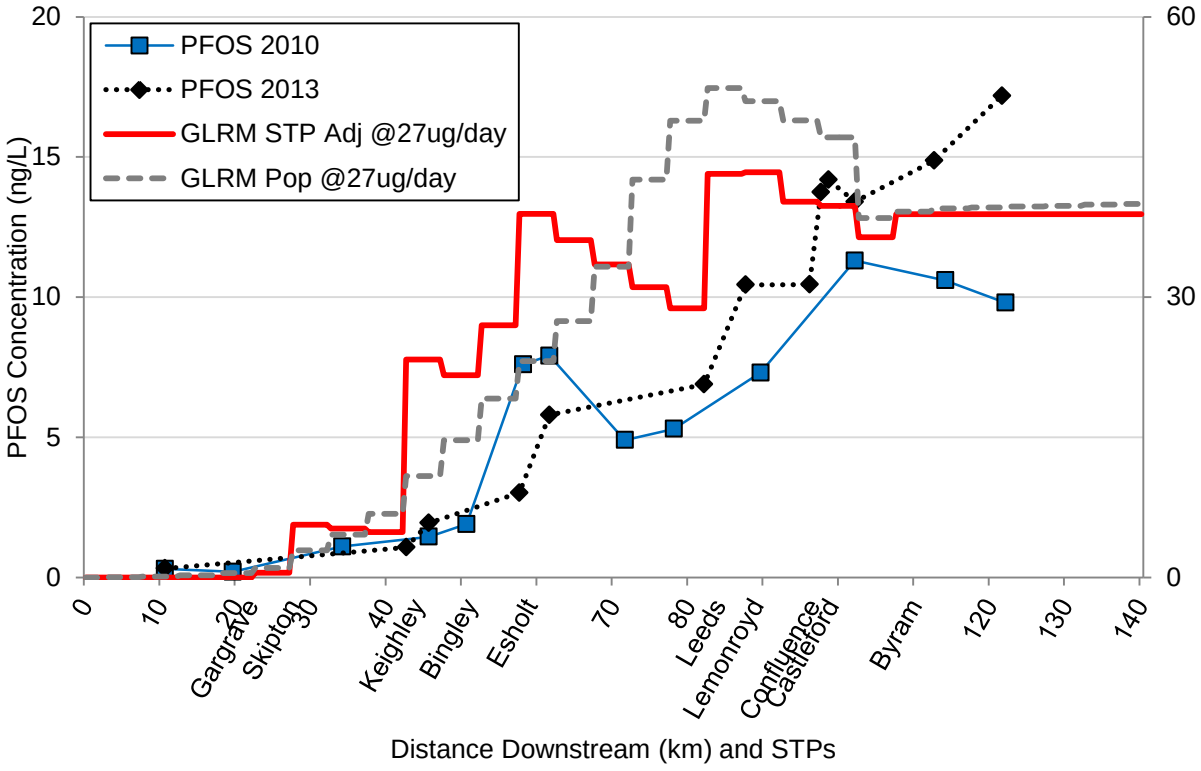

Figure 7: Measured vs modelled PFOS concentrations in the River Aire. Solid line is water concentration predicted using the STP type derived emissions and dashed line is Population derived emissions on the secondary axis to avoid distortion.

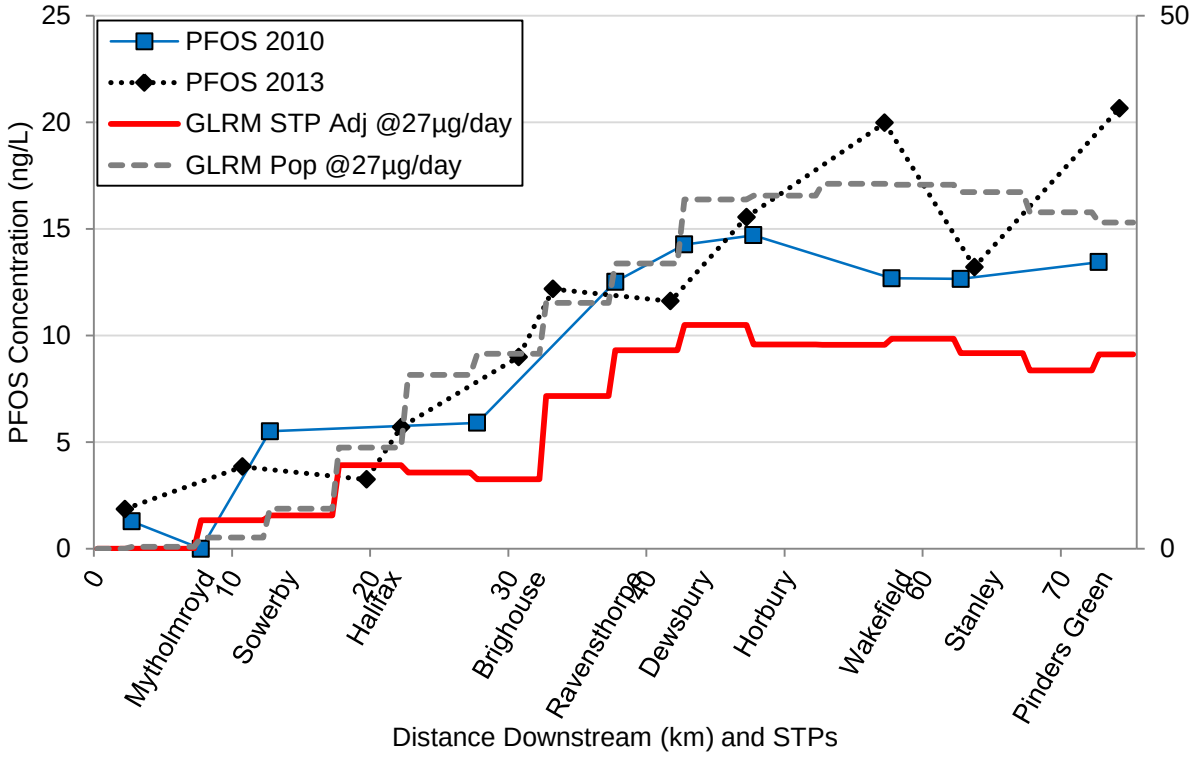

Figure 8: Measured and modelled PFOS concentrations in the River Calder. Solid line is water concentration predicted using the STP type derived emissions and dashed line is Population derived emissions on the secondary axis to avoid distortion.

3.4 Identifying the sources of PFOS

The likelihood of PFOS emissions arising from domestic effluents and subsequently discharged via STPs was assessed using sucralose analysed from the same river water samples. A comparison of measured sucralose concentrations and PFOS concentrations (Figure 4), taken from the same water samples allowed a linear regression relationship to be derived for the Aire and Calder rivers. The regression does not go through the origin, but there is a systematic difference, indicating that there is some PFOS emission that cannot be explained by population density. Figure 4 shows PFOS intercepts on the y-axis of 2 and 4.5 ng/L when sucralose concentrations are zero. This could be interpreted as a small contribution from rain, atmospheric deposition, or seepage from other sources. However, this regression relationship supports the assumption that the majority of PFOS emissions arise from STPs receiving municipal waste waters, and that PFOS emissions can therefore be mainly attributed to local population and not major industrial, fire fighting or landfill emissions.

3.5 Impact of STP type

It has been suggested in the literature that the retention of PFOS by STPs varies depending on the treatment process and complexity. Becker et al. (2008) reported that in addition to the 3 fold increase in PFOS concentrations due to precursor breakdown in the liquid phase, there was a 9 fold increase in the mass flow of the particulate phase. Although 55% of the daily mass was released into the river, the STP retained 45% of PFOS in the dewatered, deactivated sewage sludge. Interestingly, measured concentration trends within the Aire and Calder Rivers suggested that STPs with secondary activated sludge treatment emit significantly lower levels of PFOS. Emissions could be derived from concentrations measured in the river, which were linked to the closest STP and associated to population served.

A single per capita emission value will not be appropriate if there are substantial losses during the STP, or losses and/or releases from other environmental compartments. Consequently, using the EU average overestimates concentrations in the Aire and Calder. The EU average may be more applicable to larger volume rivers, flowing over greater distances, such as the River Rhine. To assess this, an effluent sample was collected from the effluent stream of Leeds STP, the largest STP on the River Aire, serving a population of nearly 600,000 people with an annual discharge of 1 million m^3/year.

The overestimation of PFOS emissions by the model around the major city of Leeds is clearly due to the type of STP. Esholt STP, close to Leeds, serves a population of approximately 300,000 people, however, it has recently undergone a series of upgrades including the addition of 204m long × 80m wide activated sludge plant and could therefore be more efficient at removal of PFOS from the liquid phase. This hypothesis is in agreement with Becker et al. (2008) and resulted in the calculation of a 4.3:1 ratio, reflecting that STPs with only trickle filters and no secondary activated sludge treatments emit approximately 4.3 times more PFOS than those with activated sludge treatments. This is most apparent in the River Aire, when the river passes through the cities of Bradford and Leeds. Here a spike in the measured concentrations in the river might be expected, but was not evident. The PFOS concentration measured in the effluent was 13.4 ng/L which corresponds to a per capita emission rate of 6.8 µg/day/person, four times lower than the EU average. Leeds STP uses activated sludge treatment so adjusting for this treatment process results in very good agreement with the hypothesis that AS treatment increases PFOS removal by 4.3 times (27/4.3 = 6.3 µg/day/person). Following this we performed two further model runs, the first

using emissions based on population served per STP at 27 µg/day/capita and the second with adjustment depending on STP type (respectively, grey dotted and solid red lines in Figure 7 and 8).

PECs based on emissions from STPs at an equal rate of 27 µg/day/capita lead to a slight improvement in absolute concentrations and the overall trend, but still overestimate MECs by a factor of 2 to 3 for both rivers. The STP type emission scenario leads to a significant improvement in PECs. In this scenario several of the updated STPs on each river emit 4.3 times less PFOS. The improvement in the River Aire PECs is reflected in both the absolute PFOS concentrations (still a slight overestimation) and the overall trend, particularly near the Esholt and Leeds STPs. The River Calder PECs have now dropped below MECs and the trend in concentration has improved.

In conclusion, the model can predict spatial trends of PFOS with reasonable accuracy, and with refinement of the model inputs based on the type and location of STPs, it can reproduce measured results very well. Therefore, it is recommended that future monitoring studies combine sampling of river water with STP effluents to better understand the influence of STP emissions on freshwater environments.

3.6 Estimated total PFOS emissions from the UK

Finally, the model was run in 'reverse' mode to calculate the inputs needed to achieve a 1:1 match between MECs and PECs. This was performed simply by adjusting inputs box by box until the PEC matched the MEC to within 0.1 ng/L and was performed for both rivers and both monitoring data sets (2010 and 2013) to produce 'best-fit' inputs. The best-fit inputs were then compared with the inputs derived from population and STP population. The best correlations were found for the STP type input (Table S1).

The total mass inputs derived for the best-fit scenario were summed to give the mass of PFOS discharged from the River Calder and subsequently the River Aire. Based on the monitoring data and our best-fit model inputs, we estimate that in 2010 and 2013, 8.9 and 12.8 kg's were discharged from the River Aire, respectively. 2.3 million people reside in the catchment area, approximately 4.1% of the UK population. Scaling up the discharge from the River Aire to the UK, we estimate the total annual mass of PFOS discharged from UK rivers to be in the region of 215 to 310 kg/year. Also, using the estimated discharges from the STP adj' and best-fit scenarios for each individual river (in kg/year) and the population in each catchment we calculate per capita emission rates. The River Calder per capita emission rate ranged

between 8 and 18.5 µg/day with a mean of 12.8 µg/day, and the River Aire ranged between 9.9 and 15.1 µg/day with a mean of 12.8 µg/day. This estimated per capita emission rate is less than half that of the 27 µg/day EU average initially used to test the model. Our monitoring results show that, despite the ban on PFOS, UK levels in freshwater have yet to show any significant decline, but total discharges remain lower than those observed in Europe, likely due to the treatment methods in use at STPs.

Acknowledgements

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Supplementary Material for Comparing Measured and Modelled PFOS Concentrations in a UK Freshwater Catchment

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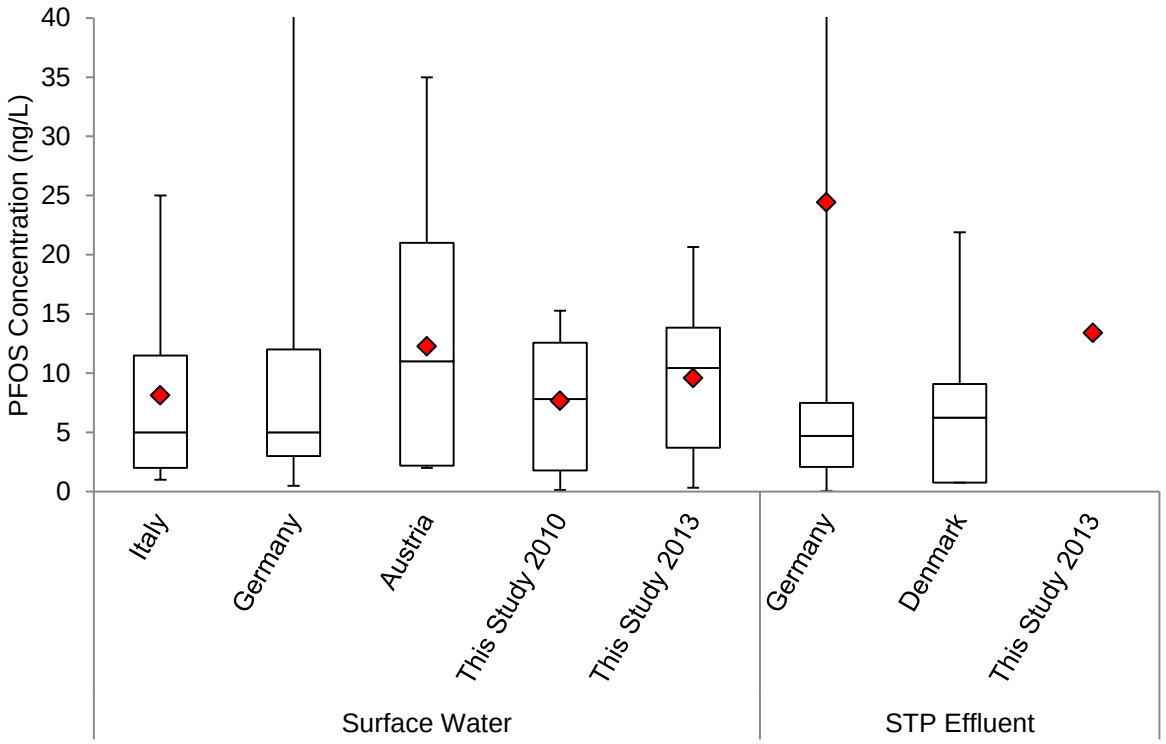

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601 **Figure S 1. Comparison of measured European surface water and STP effluent concentrations of PFOS**
602 **with data collected in this study (UK). Excluding outliers and y axis has been cropped. Mean German**
603 **surface water and Denmark STP effluent concentrations are 124 and 65 ng/L, respectively.**
604

605

606 **Table S 1. Correlation analysis of all model inputs.**

Model Input	Population	STP Pop	STP Adj'	BestFit2010	BestFit2013
Population	1				
STP Pop	0.36	1			
STP Adj'	0.12	0.16	1		
BestFit2010	0.06	-0.04	**0.97**	1	
BestFit2013	0.06	-0.06	**0.96**	**0.98**	1

r values significant at the $p < 0.01$ are in bold

607 **Table S 2. 2010 sampling location coordinates (British National Grid) with PFOS, PFOA and sucralose concentration measurements.**

Sample Label	X	Y	River	Location	Date	Time	PFOS conc' (ng/L)	Mean PFOS conc' (ng/L)	Sucralose conc' (µg/L)	PFOA conc' (ng/L)
A1, A2, A3	390417	459305	Aire	Airton	13.04.2010	09:15	0.48, 0.17, 0.25	0.2	<LOQ	2.1, 1.8, 2.0
A4	393419	454095	Aire	Gargrave	13.04.2010	09:45	0.15	0.2	<LOQ	1.7
A5	401137	445692	Aire	Kildwick Bridge	13.04.2010	10:00	1.08	1.1	0.6	2.3
A6, A7	409515	440759	Aire	Crossflats	13.04.2010	10:25	1.55, 1.37	1.5	2.0, 2.1	5.6, 6.0
A8	412248	437788	Aire	Bingley	13.04.2010	10:45	1.88	1.9	1.7	5.6
A9, A10	417934	440128	Aire	Esholt	13.04.2010	11:10	7.97, 7.17	7.6	1.4, 1.1	5.5, 7.1
A11, A12	419427	437978	Aire	Apperley Bridge	13.04.2010	12:05	8.16, 7.65	7.9	4.0, 3.7	10.2, 9.6
A13	425949	435592	Aire	Kirkstall	13.04.2010	12:45	4.88	4.9	3	9.3
A14	431392	432435	Aire	Leeds	13.04.2010	13:15	5.25	5.3	2.6	13.1
A15	438269	428035	Aire	Lemonroyd	13.04.2010	14:00	7.28	7.3	6.6	12.3
A17	445688	427185	Aire	New Fryston	13.04.2010	15:10	11.27	11.3	8.7	13.6
A18	453285	425585	Aire	Beal	13.04.2010	15:50	10.61	10.6	12.9	14.5
A19, A20, A21	457922	426170	Aire	Chapel Haddlesey	13.04.2010	16:05	9.74, 9.81, 9.85	9.8	5.8, 6.9, 7.0	12.5, 14.2, 12.6
C20, C19, C18	396442	431341	Calder	Widdop	14.04.2010	13:10	1.37, 1.04, 1.44	1.2	>LOQ	9.9, 9.2, 8.3
C17, C16	401269	425989	Calder	Mytholmroyd	14.04.2010	12:00	5.51, 5.51	5.5	0.4, <LOQ	11.6, 11.3
C15, C14	412406	422277	Calder	Elland	14.04.2010	11:40	6.06, 5.75	5.9	2.1, 2.0	14.5, 15.9
C13, C12	421563	419861	Calder	Shepley Lock Bridge	14.04.2010	11:20	12.82, 12.21	12.5	3.6, 3.1	16.6, 15.2
C11, C10	424502	421390	Calder	Thornhill Lees	14.04.2010	10:40	14.39, 14.15	14.3	10.8, 12.8	15.7, 13.5
C9, C8	428015	417960	Calder	Horbury	14.04.2010	10:20	14.12, 15.28	14.7	12.0, 15.5	19.8, 18.5
C7, C6	433833	420145	Calder	Wakefield	14.04.2010	09:50	12.58, 12.78	12.7	10.6, 10.9	18.5, 18.1
C5, C4	436476	422395	Calder	Newland Hall	14.04.2010	09:20	12.41, 12.89	12.7	15.4, 12.7	16.5, 16.2
C3, C2, C1	440969	425835	Calder	Castleford	13.04.2010	14:35	13.11, 12.57, 14.65	13.4	15.1, 12.7, 11.8	16.4, 16.5, 14.9

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609

610 **Table S 3. 2013 sampling location coordinates (British National Grid) with PFOS and sucralose concentration measurements.**

Sample Label	X	Y	River	Location	Date	Time	PFOS conc' (ng/L)	Sucralose conc' (µg/L)	Water temperature (°C)	pH
A1	390380	459217	Aire	Airton	30.04.2013	10:30	0.3 (<LOQ)	0.0	10.9	8
A2	407455	442249	Aire	Keighley Up	30.04.2013	11:20	1.1 (<LOQ)	1.7	10.8	7.8
A3	409500	440839	Aire	Keighley Down	30.04.2013	11:40	1.9 (<LOQ)	4.1	10.9	8.2
A4	417892	440091	Aire	Esholt Up	30.04.2013	12:10	3.0 (<LOQ)	4.4	11	8
A5	419429	437978	Aire	Esholt Down	30.04.2013	12:30	5.8	9.6	12.2	8.3
A6	433336	430782	Aire	Leeds Up	30.04.2013	13:20	6.9	7.6	12.1	8.2
A7	434608	430782	Aire	Leeds Effluent	30.04.2013	14:25	13.4	30.5	15	7
A8	437268	429437	Aire	Leeds Down	30.04.2013	14:50	10.4	16.3	13	7.5
A9	442338	426764	Aire	Pre Confluence	30.04.2013	15:50	10.4	13.3	13.5	7.8
A10	442800	425974	Aire	Post Confluence	30.04.2013	16:10	13.7	16.5	13	8.4
A11	444062	426779	Aire	Castleford Up	30.04.2013	16:50	14.2	12.8	13.3	8.3
A12	445639	427191	Aire	Castleford Down	30.04.2013	17:10	13.4	13.1	14.2	8.2
A13	453284	425558	Aire	Beal	30.04.2013	17:45	14.9	14.5	13.1	8
A14	457901	426155	Aire	Chapel Haddlesey	30.04.2013	18:00	17.2	14.3	13	8.2
C11	396002	431359	Calder	Widdop	01.05.2013	16:15	1.9 (<LOQ)	0.0	13.2	7.5
C10	401262	425999	Calder	Mytholmroyd	01.05.2013	15:30	3.9	1.5	11.6	8.5
C9	408450	422370	Calder	Halifax Up	01.05.2013	14:50	3.3	1.6	11.3	8.5
C8	409228	422245	Calder	Halifax Down	01.05.2013	14:30	5.7	5.3	11.7	7.9
C7	416981	421831	Calder	Brighouse Up	01.05.2013	14:10	9.0	4.3	12.5	7.5
C6	418553	420751	Calder	Brighouse Down	01.05.2013	13:50	12.2	6.2	13.5	7
C5	424546	421319	Calder	Dewsbury Up	01.05.2013	12:20	11.6	5.1	12.6	7.8
C4	428029	417944	Calder	Dewsbury Down	01.05.2013	11:50	15.6	14.5	12.7	7.2
C3	433812	420132	Calder	Wakefield Up	01.05.2013	11:15	20.0	14.9	11.6	7.5
C2	435483	423075	Calder	Wakefield Down	01.05.2013	10:20	13.2	18.5	11.6	7.3
C1	440953	425809	Calder	Pre Confluence	30.04.2013	15:20	20.7	20.8	12.2	7.8

611 **Table S 4. River Aire data used to derive model inputs.**

Box	Population	STP name	Distance downstream (km)	Type	STP Population Served	Effluent Discharge (m^3/day)	Population x 27µg/day/capita (kg/year)	STP Pop' x 27µg/day/capita (kg/year)	STP Adj' x 27µg/day/capita (kg/year)
1	263						0.00	0.00	0.00
2	422						0.00	0.00	0.00
3	1,211						0.01	0.00	0.00
4	2,040						0.02	0.00	0.00
5	5,441	Gargrave	22	TF	1,588	523	0.05	0.02	0.02
6	19,912	Skipton	28	TF	17,278	6,829	0.20	0.17	0.17
7	20,179						0.20	0.00	0.00
8	29,859						0.29	0.00	0.00
9	57,156	Keighley	45	TF	79,077	35,161	0.56	0.78	0.78
10	63,027						0.62	0.00	0.00
11	80,746	Bingley	51	TF	33,717	13,621	0.80	0.33	0.33
12	85,271	Esholt	59	AS/TF	312,826	133,444	0.84	3.08	0.72
13	101,084						1.00	0.00	0.00
14	143,138						1.41	0.00	0.00
15	232,129						2.29	0.00	0.00
16	200,002						1.97	0.00	0.00
17	161,731	Leeds	84	AS/TF	542,233	272,739	1.59	5.34	1.24
18	59,827	Lemonroyd	89	TF	27,260	8,840	0.59	0.27	0.27
19	43,281						0.43	0.00	0.00
20	50,229	Castleford	98	TF	23,539	9,074	0.50	0.23	0.23
21	65,162						0.64	0.00	0.00
22	37,130	Byram	110	TF	45,116	12,372	0.37	0.44	0.44
23	19,246						0.19	0.00	0.00
24	4,159						0.04	0.00	0.00
25	5,682						0.06	0.00	0.00
26	5,236						0.05	0.00	0.00
27	6,810						0.07	0.00	0.00
28	4,111						0.04	0.00	0.00

Continued from Table S3 above

Box	Population	STP name	Distance downstream (km)	Type	STP Population Served	Effluent Discharge (m^3/day)	Population x 27µg/day/capita (kg/year)	STP Pop' x 27µg/day/capita (kg/year)	STP Adj' x 27µg/day/capita (kg/year)
29	8,138						0.08	0.00	0.00
30	13,500						0.13	0.00	0.00
Total	**1,526,121**						**15.0**	**10.7**	**4.2**

612

613 **Table S 5. River Calder data used to derive model inputs**

Box	Population	STP name	Distance downstream (km)	Type	STP Population Served	Effluent Discharge (m^3/day)	Population x 27µg/day/capita (kg/year)	STP Pop' x 27µg/day/capita (kg/year)	STP Adj' x 27µg/day/capita (kg/year)
1	1,206						0.01	0.00	0.00
2	6,799	Mytholmroyd	8	TF	10,346	5,825	0.07	0.10	0.10
3	23,675	Sowerby	14	AS	12,419	4,775	0.23	0.12	0.03
4	56,207	Halifax	19	AS	99,213	52,367	0.55	0.98	0.23
5	77,796						0.77	0.00	0.00
6	38,034						0.37	0.00	0.00
7	78,295	Brighouse	32	AS/TF	219,946	126,234	0.77	2.17	0.50
8	76,767	Ravensthorpe	39	TF	37,357	14,055	0.76	0.37	0.37
9	122,842	Dewsbury	44	AS/TF	127,050	59,600	1.21	1.25	0.29
10	52,751						0.52	0.00	0.00
11	70,986	Horbury	50	TF	14,837	4,605	0.70	0.15	0.15
12	57,103	Wakefield	58	AS	93,726	44,095	0.56	0.92	0.21
13	49,237	Stanley	65	AS	17,636	4,762	0.49	0.17	0.04
14	24,738						0.24	0.00	0.00
15	46,575	Pinders Green	73	TF	38,267	-	0.46	0.38	0.38
Total	**783,013**						**7.7**	**6.6**	**2.3**

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Table S 6. Parameters used in the model for PFOS. Some reparameterisation was performed to adapt the model from the original by Blaser et al., (2006).

Parameter	Explanation	Unit	Value
K_d	Partitioning coefficient	-	7.5
U	Water flow velocity	m/s	1
SPM	Concentration of suspended particulate matter	kg/m^3	0.01
p_{sed}	Sediment density	kg/m^3	2500
φ	Porosity of sediment	-	0.9
u_{sed}	Settling velocity of SPM	m/s	5.79E-06
μ_{resup}	Resuspension rate	kg/m^{2}d	1.00E-04
L_{deg}	Degradation rate constant in water	1/s	0
S_{deg}	Degradation rate constant in pore water of sediment	1/s	0

Table S 7. Sensitivity analysis of the model. Concentration of PFOS in the moving water layer (L1) shows limited sensitivity to changes in the model parameters. The majority of the model parameters relate to sedimentation factors and have little or no influence on PFOS in the moving water layer.

Parameter	Explanation	Unit	Original Value	Range (±10%)	Change in Concentration L1 (%)
U	Water flow velocity	m/s	1	0.9 - 1.1	$^{+}$10 - $^{-}$10
SPM	Concentration of suspended particulate matter	kg/m^3	0.01	0.009 - 0.011	0
p_{sed}	Sediment density	kg/m^3	2500	2250 - 2750	0
φ	Porosity of sediment	-	0.9	0.81 - 0.99	0
u_{sed}	Settling velocity of SPM	m/s	5.79E-06	5.21E-06 - 6.37E-06	0
μ_{resup}	Resuspension rate	kg/m^{2}d	1.00E-04	9.00E-05 - 1.10E-04	0